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TECHNICAL REPORT

By

R. H. Wolff

June 1966

U. S. ARMY WEAPONS COMMAND

ROCK ISLAND ARSENAL RESEARCH & ENGINEERING DIVISION

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HYDROGEN EMBRITTLEMENT OF STEEL IN METAL FINISHING PROCESSES OF BLACK OXIDE AND ZINC PHOSPHATIZE

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R. H. Wolff
Laboratory Branch

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PEMA Project No. 56228 AMS Code 4230.15.6228.20.01

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ABSTRACT

Static load tests were conducted with notched, steel tensile specimens after processing in black oxide (specification MIL-C-13924 Class [illegible]) and also after processing in zinc phosphatize solution (specification MIL-P-16232C Type Z), to determine embrittlement characteristics of these processes.

The scope of work was limited to a brief survey to determine whether the problem was serious for these processes. Results based on the use of types 4140, 1045 and 1095 steel specimens at hardness of Rockwell C 50 show that embrittlement is not a problem with the black oxide process. The zinc phosphatize process is critically embrittling, and relief treatment for higher strength steels is advisable.

FOREWORD

This work was undertaken as a part of a Production Engineering Measure on Process Improvement, Pron No. M1-3-23042-01-M1-M5 and AMC Code 4230.15.6228.20.01. The project title was Manufacturing Chemistry and the project number was 56228.

The work was intended to supply an answer to the question of whether hydrogen embrittlement is induced to a damaging level in high strength steel in the production of black oxide coatings, and zinc phosphatize coatings.

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PROBLEM

To determine the susceptibility of hardened steel to hydrogen embrittlement in black oxide and zinc phosphatizing processes.

BACKGROUND

High strength steels periodically fail in service where conditions offer no apparent reason for such a failure. Under metallurgical examinations, some of these failures are solved by evidence of improper heat treatment, or material inadequacies. Some of the materials show no reasons for metallurgical failure, but perhaps were previously treated in a metal finishing process. These pieces become candidates for "delayed failure by hydrogen embrittlement."

In electrodeposition and pickling operations, atomic hydrogen is produced at the surface of the basis metal, where it is readily absorbed. Steels are more or less susceptible to embrittlement by hydrogen absorption depending upon their analysis and metallurgical history. The nature of the embrittlement is not understood, but at least in part it is the result of interference of the hydrogen atoms with the normal flow or slip of the lattice planes under stress.(1) It appears that there are no ferritic steels that are immune to hydrogen embrittlement.(2) The embrittlement occurs at all strength levels, but is usually most severe at what is termed ultra high strength levels, 200,000 psi and above.

Of the nonferrous metals and alloys, only titanium and zirconium are known to be susceptible to damage from hydrogen that might come from metal finishing operations.(3)

There is little or no apparent agreement on what causes hydrogen embrittlement, on methods of testing for embrittlement, or on ways of avoiding or removing the hydrogen absorbed.(4) There is also no precise guidance or recommended practice to define the situation for the user of these products. Specifications often include a provision to the effect that after all metal finishing operations are finished, the steel shall be "free from the detrimental effects of hydrogen embrittlement." It has long been assumed in the military specifications that steels having a hardness of Rockwell C 40 or above are subject to critical hydrogen embrittlement. This hardness has become a traditional figure which is introduced into almost every specification related to the production of finishes on steel. In some cases the processes are operated under conditions that according to present knowledge would appear to minimize hydrogen uptake. Among these processes is that of black oxide coating of steel (specification MIL-C-13924). The

coating is formed in a hot alkaline oxidizing solution which does not provide an atmosphere conducive to hydrogen sorption into steel.

A second case of questionable understanding is that of specification MIL-P-16232C, Phosphate Coatings, Heavy, Manganese or Zinc Base (For Ferrous Metals). This specification requires consideration of embrittlement relief for minimum hardness of Rockwell C 39 for alloy steels and C 47 for carbon steels. Suggested relief treatment is eight hours bake at 210° to 225°F., or room temperature aging for 123 hours. Most specifications do not make this distinction between steel types.

With these examples of confusing background, an experiment was undertaken to determine whether a black oxide process would embrittle, and whether the remedial action of baking for eight hours at 210°F. is sufficiently well defined for the phosphatize process.

APPROACH AND RESULTS

The scope of this work was limited to review the need for control of hydrogen embrittlement relief of steel processed with black oxide coatings, and heavy phosphate coatings as provided in Military Specifications MIL-C-13924 and MIL-P-16232.

Several steels were selected and prepared as notched tensile specimens (see Figure 1) for use in static load test. This test is favored for evaluation of hydrogen embrittlement because it gives the most reproducible results.[5] The test is conducted by subjecting the prepared notched specimen to a dead weight tensile load equal to 75% of the ultimate notched tensile strength of the steel. The specimen is expected to successfully support the load for a minimum of 200 hours without failure by breaking or showing signs of cracks. The load is applied by a lever arm advantage so that even though some relaxation occurs in the system, the load remains the same.

A number of representative low alloy steels were planned for long range use. However, present tests were accomplished with only three types. These types were 1045, 1095 and 4140, conforming to the requirements of specification QQ-S-624, Steel Bar, Alloy. All specimens were heat treated to provide a hardness level of Rockwell C 50.

Notched Tensile Specimen

Length	4 inches
Diameter	1/2 "
Finished gauge diameter	0.357
Notch root diameter	0.225
Notch root radius	0.025

FIGURE 1

BLACK OXIDE PROCESS

The first phase of test work was conducted with specimens coated with the black oxide as formed in the conventional alkaline oxidizing process (Class 1 of specification MIL-C-13924A, Coating, Oxide, Black, for Ferrous Metals).

The black oxide solution was prepared by dissolving RIA Salt #5 (composition approximately two parts sodium hydroxide and one part sodium nitrate) in the proportion of eight pounds per gallon of water (960 gm/liter). Final adjustment to set the operating temperature range of 270° to 290°F. was made by small additions of Salt #5 to make a working volume of about half a gallon. Temperature control was then accomplished by periodic small additions of water while the bath was in use. The temperature rises as the water is evaporated and the solution becomes more concentrated.

Unless otherwise specified, all the tests were run with specimens that were vapor degreased and treated for five minutes to electrolytic alkaline derusting. The derusting was done with a DC current periodic reversal cycle of ten seconds cathodic action and five seconds anodic action as a standard procedure. To provide the presence of hydrogen during pretreatment, some of the specimens were pickled for five minutes in one to one hydrochloric acid. Other specimens were cathodically charged for five to ten minutes in 20% sulfuric acid at a current density of approximately 30 ma/sq.cm.

Black oxide coatings were produced in 30 minutes at temperatures of 265° to 285°F., and immediately upon removal from the coating process, the specimens were subjected to the static load test.

No failures were experienced as a result of these operations. All specimens successfully completed 200 hours of static load test.

A test was then processed in the black oxide solution to which 0.32 oz/gal sodium cyanide had been added. Again no failure resulted from the 200 hour static load test. The test results are recorded in Table I.

TABLE I

BLACK OXIDE COATED TESTS IN STATIC LOAD

Test No.	Steel Type	Tensile Load x1000 psi	Pretreatment	Result 200 Hours
1	1095	231	5 minutes 1-1 HCl	OK
2	1095	231	" " " "	OK
3	1095	231	10 minutes cathodic*	OK
4	1095	231	" " "	OK
5	4140	296	5 minutes cathodic	OK
6	4140	296	" " "	OK
7**	4140	296	" " "	OK

* In 20% Sulfuric Acid
** Cyanide added to black oxide solution, 0.32 oz/gal (2.4 g/l.)

PHOSPHATIZING PROCESS

In the second phase of the work, zinc phosphate coatings were applied for test of the embrittling effects of this process. Tests under this part were conducted on two carbon steel types, 1045 and 1095. Specimens were heat treated to a hardness of Rockwell C 50, and two surface conditions provided. For one condition the surface was as prepared by grinding in the specimen manufacture. For the second condition the surface was steel grit blasted (80 grit) just prior to the application of the phosphate coat. Unless specifically mentioned, the specimens were not abrasive blasted. Specimens were prepared by vapor degreasing and a five minute treatment in electrolytic alkaline derusting solution as previously described for the black oxide pretreatment.

The phosphatizing process was a conventional hot, zinc based solution having a nominal control range of 27 points* total acid, and processing time of 30 minutes. Tests were conducted immediately after processing except where baking for hydrogen embrittlement relief was carried out. Baking time and temperature were based upon those defined in the specification, namely, eight hours at 210^{o} to 225^{o}F. for carbon steel of minimum hardness Rockwell C 47. The alternate treatment is 128 hours aging at room temperature.

* A point is equal to one milliliter of 0.1 normal sodium hydroxide solution in titrating a 10 ml sample to a phenolphthalein end point.

Part way through the tests of the 1095 type steel, a second batch of specimens was prepared by heat treatment. These specimens were from the same initial steel quantity. However, the second batch heat treatment resulted in a higher strength by approximately 10,000 psi at the testing level. Test results are recorded in Table II.

Specimens tested immediately after processing on the unblasted surfaces failed in every case. For the 1095 steel, eight hours of baking time at 210°F. was not adequate for embrittlement relief except where the surface had been abrasive grit blasted. For the unblasted surfaces, the 24 hour bake was unsatisfactory also, since tests could go either way.

To provide a satisfactory relief of embrittlement of 1045 steel, unblasted surfaces required 48 hours of baking at 210°F. The abrasive blasted test was satisfactory at 24 hours of baking at 210°F.

An air aging for 128 hours was not adequate relief for the 1045 steel

DISCUSSION

The absence of failures among tests of black oxide coated specimens offers objective evidence that this process does not contribute to the hydrogen embrittlement of the materials tested. It is believed that the nature of the process, being both alkaline and operated hot, would reduce hydrogen embrittlement rather than increase it. This would result in relieving, to a large degree, any embrittlement that had been sustained during a pretreatment such as acid pickling or cathodic cleaning. These pretreatments are not always used prior to black oxide processing, particularly where the parts are bright and clean metal, but since they might be used, pickling and cathodic charging with hydrogen were provided in these tests. If the black oxide bath is a promoter of hydrogen embrittlement it would have shown up under these circumstances.

Sodium cyanide is often added to a black oxide bath to prevent nonferrous contaminants, such as copper, from discoloring the black oxide coating. Sodium cyanide was used in these tests to insure that the addition did not alter the operating characteristics of the solution. There is a common opinion that cyanide ions are instrumental in promoting the absorption of hydrogen in steel. If this is the case, it is more likely to apply to electrolytic operations where the hydrogen is already available at the cathode surface. Since the black oxide process involves no current the cyanide is not considered likely to have any

TABLE II

ZINC PHOSPHATIZE COAT PROCESS TESTS IN STATIC LOAD
All Specimens Processed for 30 Minutes

Test No.	Steel Type	Tensile Load x1000 psi	Abrasive Blasted	Bake at 210°F.	Failure
1	1095	231	no	none	Immediate*
2	1095	231	no	none	Less than 16 hrs.
3	1095	231	no	none	Immediate
4	1095	231	no	16 hrs.	48-96 hrs.
5	1095	231	no	24 hrs.	144 hrs.
6	1095	231	yes	8 hrs.	OK @ 200 hrs.
7	1095	231	no	aged 128 hrs.	OK @ 200 hrs.
8	1095	231	no	24 hrs.	OK @ 200 hrs.
9	1095	241	no	none	Immediate
10	1095	241	no	8 hrs.	Immediate
11	1095	241	no	16 hrs.	Immediate
12	1095	241	no	24 hrs.	OK @ 200 hrs.
13	1095	241	yes	none	OK @ 200 hrs.
14	1045	270	no	none	Immediate
15	1045	270	yes	none	1/2 hr.
16	1045	270	no	8 hrs.	Less than 16 hrs.
17	1045	270	yes	8 hrs.	Immediate
18	1045	270	no	24 hrs.	96 hrs.
19	1045	270	yes	24 hrs.	OK @ 200 hrs.
20	1045	270	no	48 hrs.	OK @ 200 hrs.
21	1045	270	no	aged 128 hrs.	Immediate

* Less than 1/2 hr.

effect in the relatively small concentrations used.

Based on the admittedly small sample, the survey results show that no relief of hydrogen embrittlement effects was needed. Until hydrogen embrittlement failures occur as a traceable result of the black oxide process, a specification provision requiring lengthy procedures for relief does not appear to be warranted.

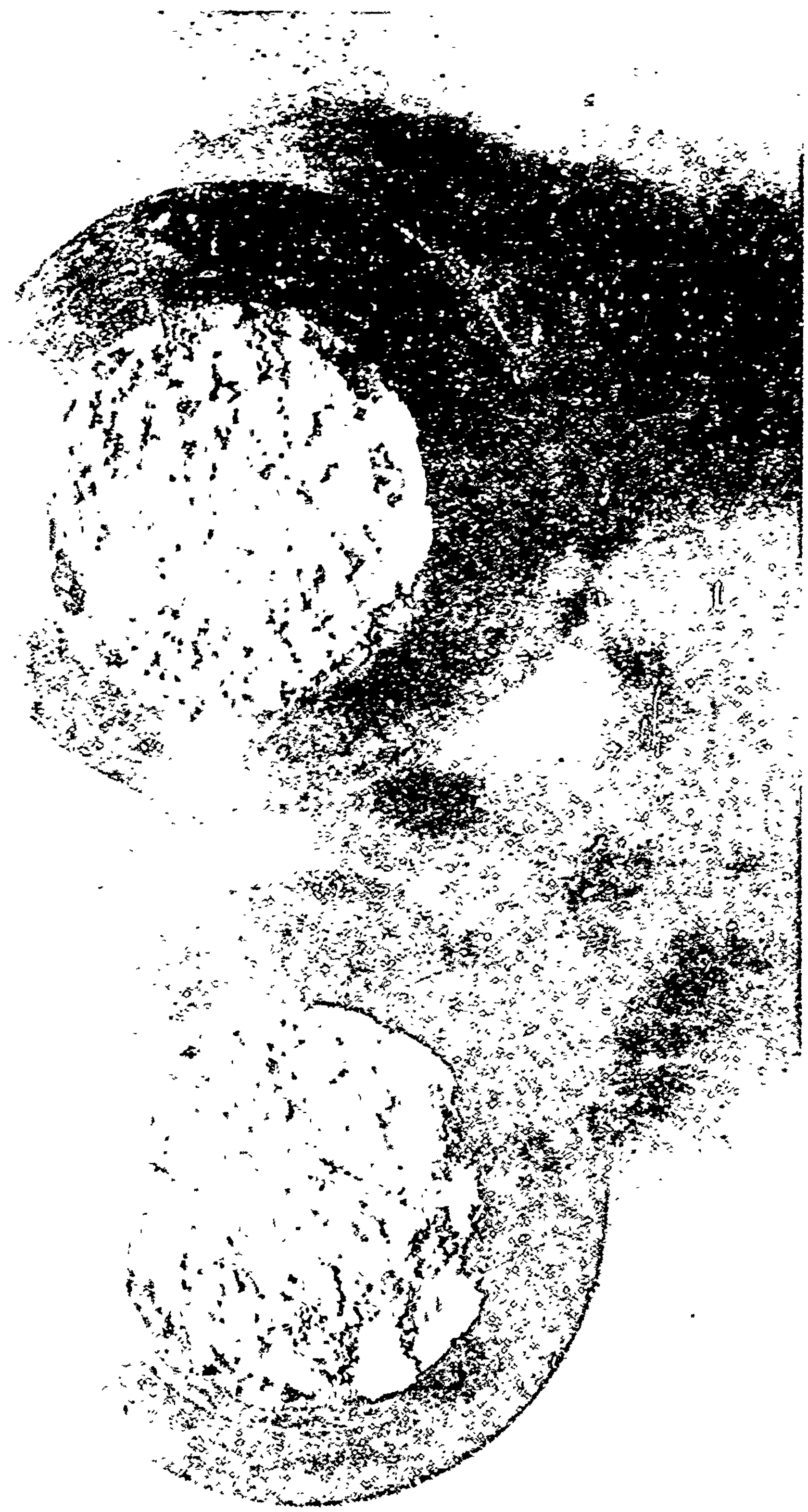
The failures experienced with the application of the zinc phosphate coating leave little doubt that the process produces a damaging level of hydrogen embrittlement. The presence of such a level is not in itself the problem, once it is known to be present. The problem is whether the level can be reduced to a non-critical stage before a load is applied that results in a delayed catastrophic failure.

The relief of hydrogen embrittlement is partially related to the nature of the coating applied. If the coating is dense and nonporous, the escape of hydrogen may be difficult. If the coating is open and porous the release of hydrogen is a matter of time and temperature. This statement of the relief mechanism is over-simplified, since a great many other factors may enter in, but it will suffice to indicate that the phosphatized surface is conducive to the release of hydrogen.

It is probable that abrasive blasting the surface just prior to processing has a beneficial effect in producing a slightly compressive surface stress and increasing the surface area, which facilitates rapid release of the absorbed hydrogen. This is suggested by the fact that the blasted tests resulted in better performance in the static load test as compared to the unblasted.

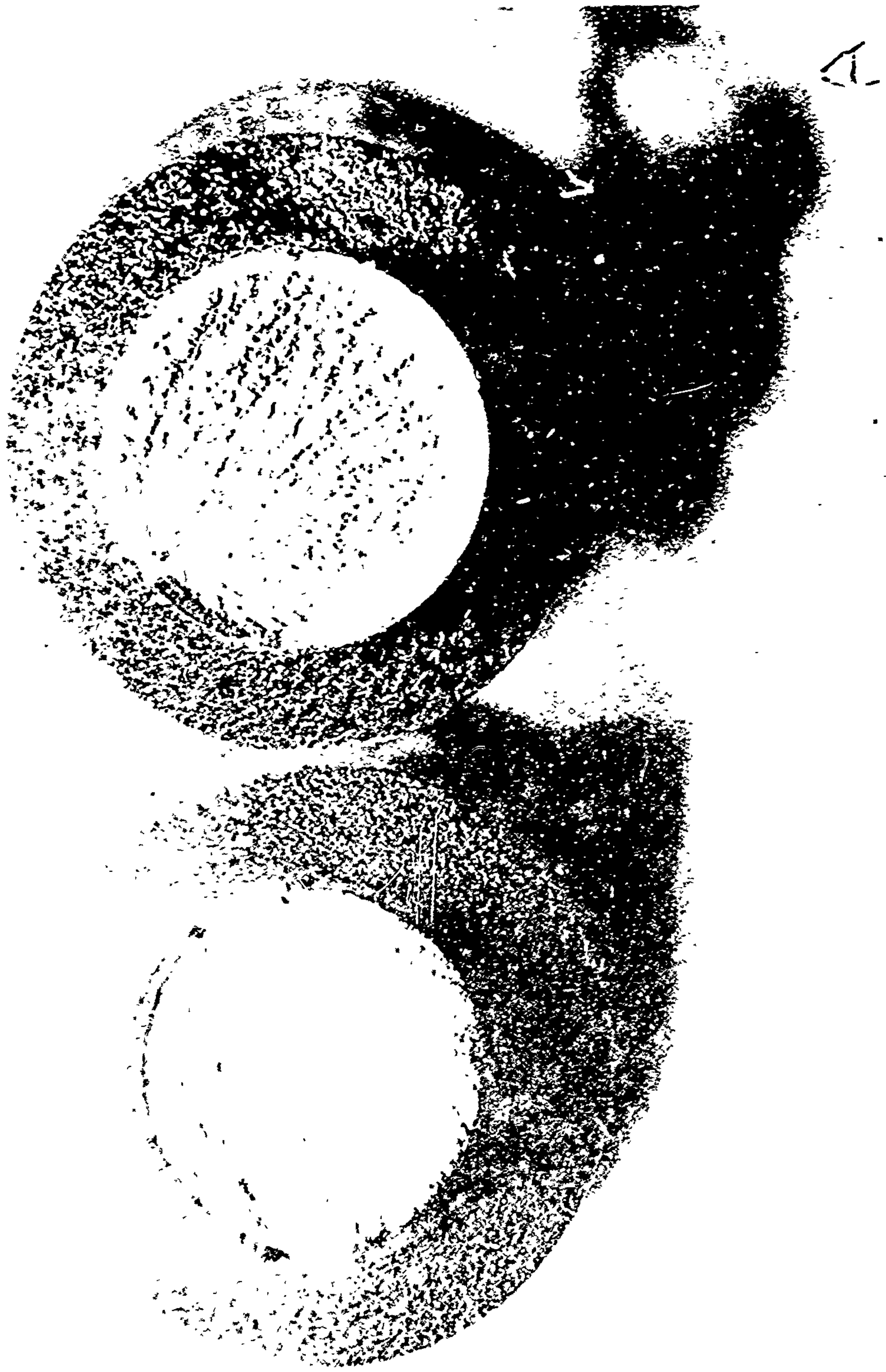
In general, articles for heavy phosphatizing are subjected to abrasive blasting, however, this procedure is not followed universally. The results indicate that relief requirements for the two surface treatments are different. The blasted surface is relieved in a much shorter time.

A series of photographs were taken of the specimen fracture surfaces of the 1045 type steel. All pictures were taken at 10X magnification. Figure 2 shows the fracture resulting from one of the untreated specimens used to determine the ultimate tensile strength. Figures 3 and 4 compare a specimen tested immediately after processing and one that was baked for eight hours at 210°F. Breaking load for the specimen in Figure 2 was 395,000 psi, and the static load applied to the static test (Figures 3 and 4) was 270,000 psi.



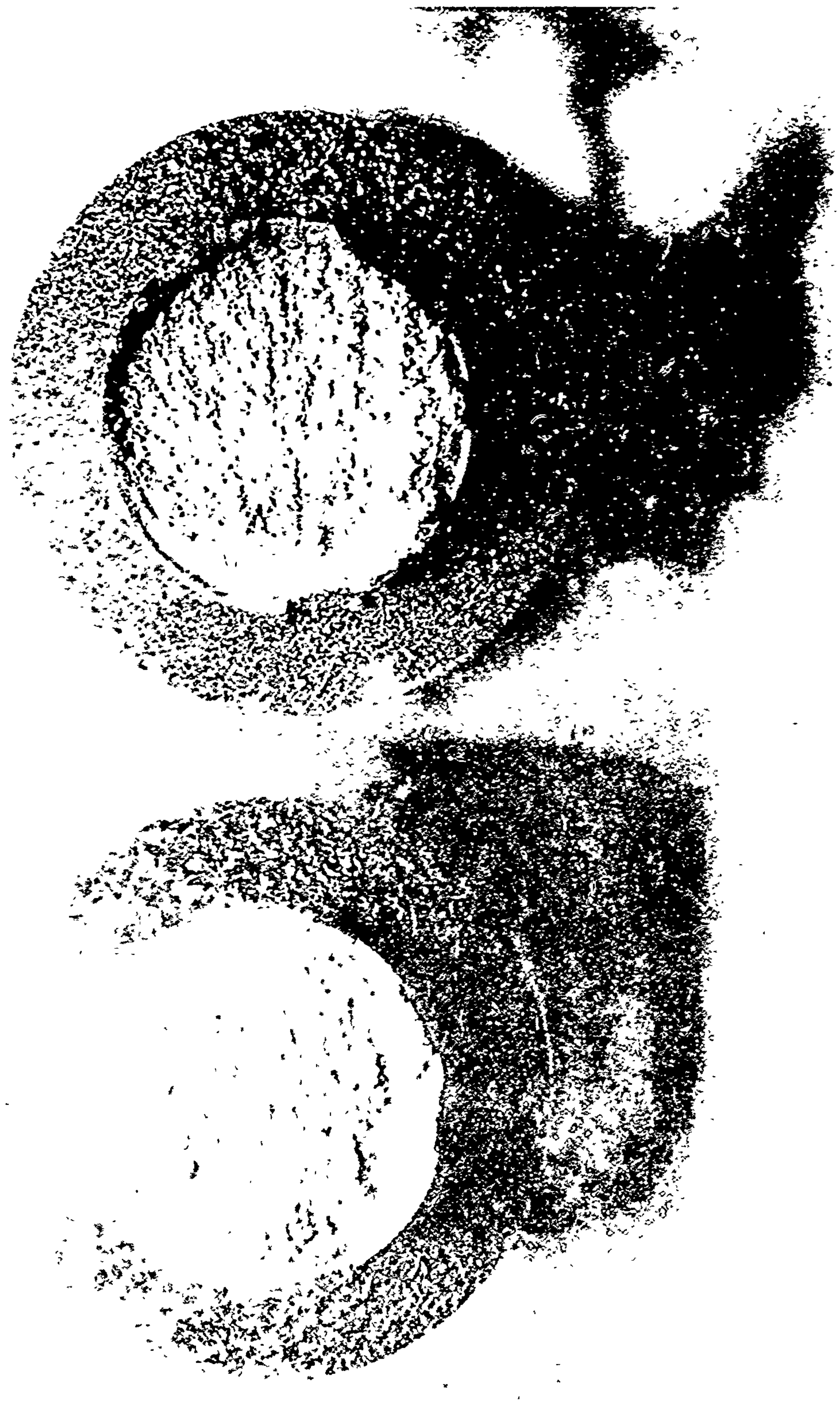
1045 STEEL. FRACTURE SURFACE FROM TENSILE STRENGTH DETERMINATION ON UNTREATED SPECIMEN. (Rc 50 HARDNESS) ULTIMATE STRENGTH 395,000 PSI

FIGURE 2



1045 STEEL UNBLASTED SURFACE PHOSPHATE COATED. FRACTURE WITH 270,000 PSI LOAD

FIGURE 3



1045 STEEL UNBLASTED SURFACE PHOSPHATE COATED,
BAKED 8 HOURS @ 210°F. 270,000 PSI LOAD

FIGURE 4

Note that in the case of the static load failure, the fracture appears to radiate from an edge. This would suggest that a nucleation site initiated at a point and then rapidly spread to the fracture.

Although very little can be safely inferred from these fractures, it is interesting to note the lip sizes of the blasted surface specimens as compared to the unblasted. (Compare Figures 5 and 6 with Figures 3 and 4) Since there is practically no elongation with a specimen of this type the cup shaped lip is sometimes considered as a suggestion of a small amount of ductility. The longer lip should be evidence of greater ductility, but is not significant in this case since both specimens broke However, significance may enter into the ultimate conditions with regard to time and temperature needed to accomplish relief for the two surface treatments.

This work has shown that even on the small scale approach to the embrittlement problem there are many areas needing clarification. No blanket recommendations can be made that will fit all situations for adequacy and be compatible with economy. It is indicated that relief is not needed for black oxide coating in the hot alkaline process. It is also apparent that the prescribed treatment for relief of phosphatized work is not completely effective. Among the unresolved questions is that of time If the baking time is extended to several days, is it not more sensible and economical to air age for a week? This would require that the pieces not be assembled or loaded in tensile stress until the aging period was accomplished.

CONCLUSIONS

Hydrogen embrittlement does not pose a problem in the hot alkaline oxidizing black oxide process for steel.

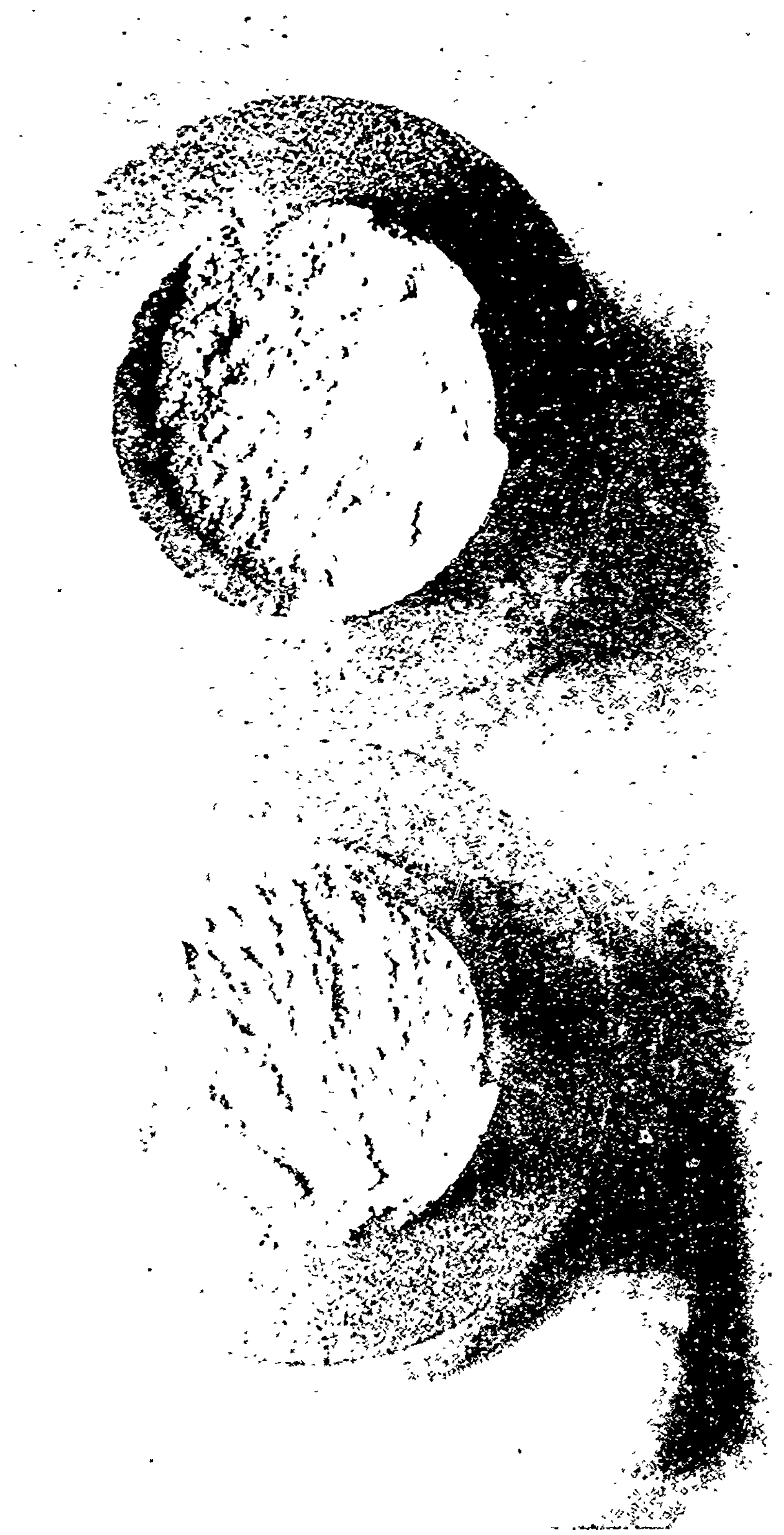
The baking time of eight hours at 210°F. did not provide reliable relief from critical hydrogen embrittlement effects for the steels and conditions tested.

RECOMMENDATIONS

It is recommended that:

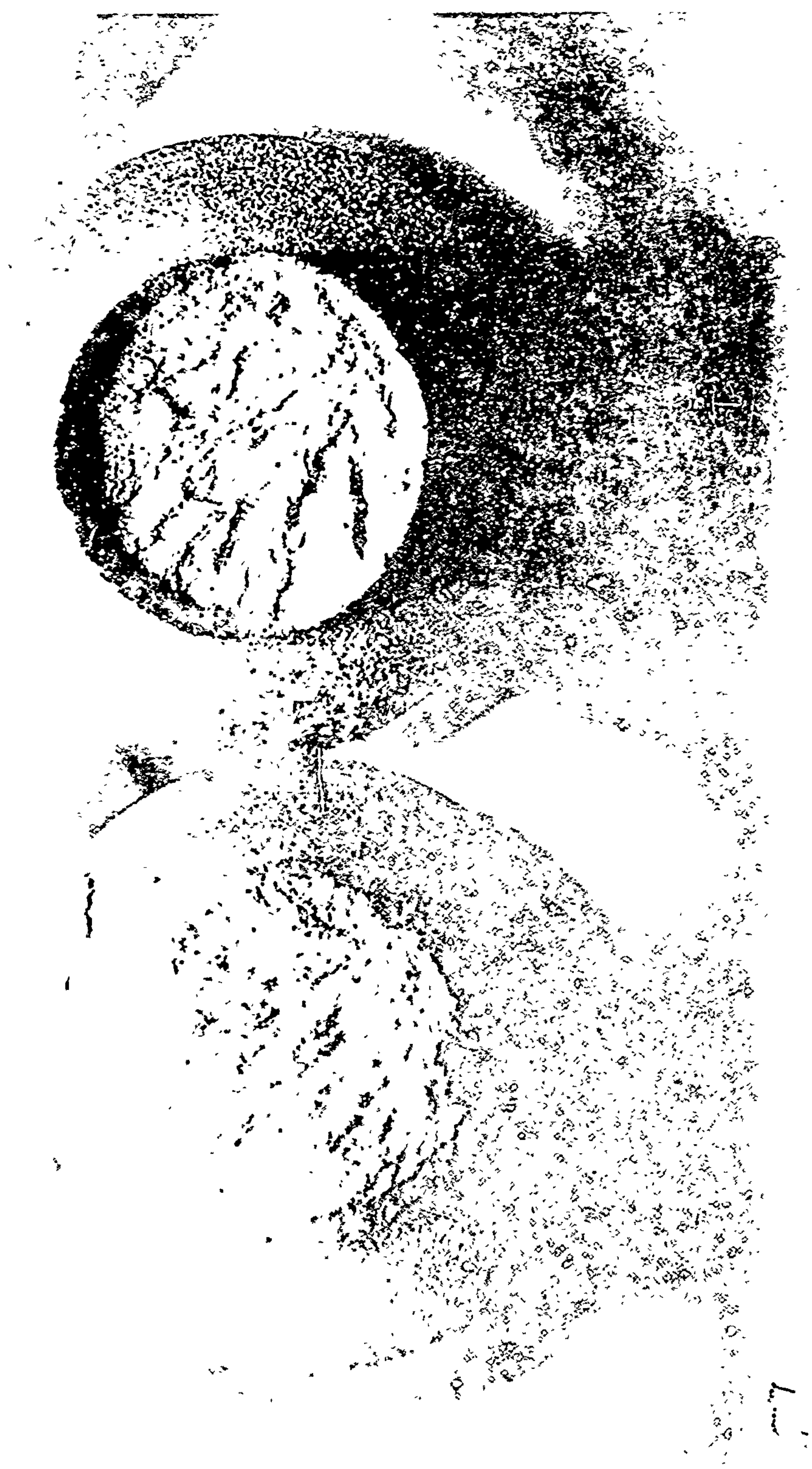
Requirements for embrittlement relief of black oxide coated steel processed in hot alkaline oxidizing solutions be dropped.

Relief for phosphatizing processes be given closer study to clarify the extent and type of treatment needed to give minimum safe levels for use.



1045 STEEL BLASTED SURFACE PHOSPHATE COATED.
FRACTURE IN 30 MINUTES 270,000 PSI LOAD

FIGURE 5



1045 STEEL BLASTED SURFACE PHOSPHATE COATED,
BAKED 8 HOURS @ 210°F. FRACTURE LESS THAN 5 MINUTES
WITH 270,000 PSI LOAD

FIGURE 6

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13 ABSTRACT

Static load tests were conducted with notched, steel tensile specimens after processing in black oxide (specification MIL-C-13924 Class 1) and also after processing in zinc phosphatize solution (specification MIL-P-16232C Type Z), to determine embrittlement characteristics of these processes. The scope of work was limited to a brief survey to determine whether the problem was serious for these processes. Results based on the use of types 4140, 1045 and 1095 steel specimens at hardness of Rockwell C 50 show that embrittlement is not a problem with the black oxide process. The zinc phosphatize process is critically embrittling, and relief treatment for higher strength steels is advisable. (U) (Author)

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